The Adverse Effects of Le Châtelier's Principle on Teacher Understanding of Chemical Equilibrium

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Chemistry education researchers have noted the inadequacy of Le Châtelier's principle (LCP) for decades *(1–12)*. They have shown how apparently reasonable applications of LCP can result in incorrect predictions about the effects of changes in concentration, volume, pressure, or temperature on chemical systems at equilibrium. Because LCP has no value for chemistry teachers and students other than historical interest, some researchers *(13–19)* have criticized the over-emphasis of LCP in the school chemistry curriculum. They have recommended the use of the equilibrium law, reaction quotient, and van't Hoff equation to predict the direction in which a chemical equilibrium system will shift when it is disturbed. Yet little progress has been made to delete LCP from the school chemistry curriculum. Textbooks of high school chemistry or college chemistry published in many countries such as the United States, the United Kingdom, Australia, Canada, and China still rely on LCP as the major predictive tool. Le Châtelier himself described three different statements of LCP *(18)*. Petrucci, Harwood, and Herring *(20)* emphasized that it is hard to state LCP unambiguously, but they believed that the essential meaning of LCP is as follows:

> When an equilibrium system is subjected to a change in temperature, pressure, or concentration of a reacting species, the system responds by attaining a new equilibrium that *partially* offsets the impact of change (*20,* p 641; emphasis in original).

However, predictions based on the above version of LCP may conflict with experimental facts. For example, if the number of moles of products in a balanced chemical equation for a gaseous equilibrium system is not equal to the number of moles of reactants, adding more reactant at constant pressure and temperature may further raise rather than partially offset the increase in concentration of that reactant *(21)*. In fact, any version of LCP may result in incorrect predictions if finite rather than infinitesimal changes in equilibrium systems are considered *(22–24)*.

Researchers have presented convincing arguments for deleting LCP from the school chemistry curriculum. But why has little progress been made? There are at least two possible reasons. First, people working in the field of chemistry education are generally unaware of the inadequacy of LCP. These people include chemistry teacher educators, chemistry officers in examination boards, members of curriculum development committees, textbook writers, and school teachers. Second, some chemistry educators may recognize the inadequacy of LCP, but they do not understand the seriousness of the consequences caused by the inclusion of LCP in the school chemistry curriculum. They believe that nothing is perfect and therefore it is acceptable that LCP has limitations. They argue, erroneously in my view, that LCP is still a useful qualitative tool to predict changes in equilibrium systems if the changes are restricted to one variable.

My experience with teacher training gained over the past decade shows that the misleading information presented by textbook writers can cause school teachers to hold misconceptions about chemical equilibrium. This is critically important because teachers cannot help their students understand what they themselves do not understand. But in the past, researchers' interest has centered on student misconceptions and has neglected teacher misconceptions. To my knowledge, only four previous studies *(18, 25–27)* assessed how LCP affects teacher understanding of chemical equilibrium. Although these four studies are useful, they have not documented the nature of teacher misconceptions in detail. The aim of my study was to identify and classify the misconceptions about chemical equilibrium held by secondary school teachers in Hong Kong.

The Hong Kong Study

In Hong Kong, secondary schooling consists of seven years (secondary 1–7), and chemistry is offered as a separate subject to secondary 4–7 students (approximately 16–19 years of age). The principles of chemical equilibrium are taught by teachers in secondary 6. A misconception test was developed to assess whether secondary school teachers understand the inadequacy of LCP. The test consisted of the following three chemical equilibrium problems:

Problem 1: The reaction

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g) \quad (1)$$

is at equilibrium in a reactor fitted with a movable piston. If a small amount of $CS_2(g)$ is suddenly added to the equilibrium mixture at constant temperature and pressure, what will happen to the number of $CH_4(g)$ molecules when equilibrium is re-established? Give reasons for your answer.

Problem 2: The reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad (2)$$

is at equilibrium in a reactor fitted with a movable piston. What will happen if some argon gas is added to the equilibrium mixture at constant pressure and temperature? Give reasons for your answer.

Problem 3: The reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad (3)$$

is at equilibrium in a syringe. If the volume is decreased at constant temperature by moving the plunger, will the concentration of $NO_2(g)$ be higher or lower than the original concentration when equilibrium is re-established? Give reasons for your answer.

The first and second problems were adapted from Cheung *(14)* while the third problem was adapted from Quílez *(18)*. Ideal gas behavior was assumed to analyze these problems. In 2007, I invited a convenience sample of 33 secondary chemistry teachers to respond to the three problems when they attended a seminar at my university. Their teaching experience ranged from 1 to 19 years, with a mean equal to 7.8 years. Seventeen teachers were female. All the teachers had a B.S. degree with a major in chemistry. The test was anonymous and lasted for 15 minutes.

The answers given by the teachers were analyzed and the different types of explanation offered by them formed the coding categories in this study. A research assistant and I coded the teacher responses together. For each answer sheet, we compared and discussed the allocation of codes until a consensus was reached.

Results and Discussion

The coding results of the first equilibrium problem are shown in Table 1. Few of the 33 teachers applied the equilibrium law to solve the first problem. Twenty-eight of the 33 teachers predicted that the number of CH_4 molecules will increase and nine of them (Code 1B1) put down LCP as their sole source of explanation. Eight teachers (Code 1B2) also appeared to apply the "change-then-offset" logic of LCP even though the name of the principle was not spelled out. Actually, LCP cannot solve the first equilibrium problem. If LCP is applied, the position of equilibrium must shift to the product side to offset the impact of addition of CS_2 gas. However, the addition of CS_2 gas will increase the total volume of the system. Instantaneously, the concentration or partial pressure of CS_2 will increase but the concentration or partial pressure of H_2 will decrease. Thus, if LCP is applied, these two changes in concentration or partial pressure must lead to opposite equilibrium shifts. Unfortunately, LCP offers no way of deciding which direction of equilibrium shift will result.

Only three of the 33 teachers answered the first equilibrium problem correctly (Code 1A1). They first wrote the reaction quotient, Q_c, expression as follows:

$$Q_c = \frac{\left(\frac{n_{CH_4}}{V}\right)\left(\frac{n_{H_2S}}{V}\right)^2}{\left(\frac{n_{CS_2}}{V}\right)\left(\frac{n_{H_2}}{V}\right)^4} = \frac{n_{CH_4}\, n_{H_2S}^{\;2}\, V^2}{n_{CS_2}\, n_{H_2}^{\;4}} \qquad (4)$$

where V is the total volume, n_{CH_4} is the number of moles of CH_4, and so on. Then, the three teachers pointed out that if CS_2 gas is added at constant pressure and temperature, both the number of moles of CS_2 and the total volume must increase. Therefore, the new position of equilibrium will depend upon the ratio, V^2/n_{CS_2}, in the above reaction quotient expression. If the new V^2/n_{CS_2} ratio is greater than the original ratio in the K_c expression, then Q_c is greater than K_c and the equilibrium position must shift to the reactant side. If the new ratio is less than the original ratio, then Q_c is less than K_c and the equilibrium position must shift to the product side.

Four teachers (Code 1B5) did try to apply the equilibrium law, but they just focused on the change in concentration of CS_2 and forgot to consider the changes in volume and the concentrations of other chemical species. One possible reason is that few textbooks discuss this kind of constant-pressure case. Another possible reason is that in gaseous equilibrium systems, the equilibrium law is often expressed as K_p rather than K_c in many textbooks. Some teachers may not recognize that the concentrations of gaseous species can be expressed as mol/L; that is, moles of gaseous species per liter occupied. Only one teacher (Code 1D1) erroneously predicted a left shift in the equilibrium

Table1. Coded Responses to the First Equilibrium Problem

Code	Teacher Response	Number of Teachers
1A1	The position of equilibrium can be shifted to the reactant or product side, depending upon the initial amount of CS_2 in the mixture. The K_c or Q_c expression is applied correctly to predict equilibrium shift.	3
1B1	Number of CH_4 molecules will increase. LCP predicts that the equilibrium will shift to the right to oppose the change/to minimize the effect of addition of CS_2.	9
1B2	Number of CH_4 molecules will increase. Because the number/concentration of CS_2 molecules will increase, the equilibrium will shift to the right to oppose/minimize such a change.	8
1B3	Number of CH_4 molecules will increase because more reactants are available to form the product CH_4.	1
1B4	Number of CH_4 molecules will increase. Because the concentration of CS_2 is increased, the position of equilibrium will shift to the right.	4
1B5	Number of CH_4 molecules will increase. Addition of CS_2 will mean that, momentarily, the ratio $[CH_4][H_2S]^2/[CS_2][H_2]^4$ is smaller than K_c and thus the position of equilibrium will shift to the right.	4
1B6	Number of CH_4 molecules will increase. Addition of CS_2 shifts the position of equilibrium to the right because the rate of the forward reaction will increase but the rate of backward reaction will remain unchanged.	1
1B7	Number of CH_4 molecules will increase. The equilibrium shifts to the right. No further explanation.	1
1C1	Number of CH_4 molecules will remain unchanged because the temperature is kept constant.	1
1D1	Number of CH_4 molecules will decrease. The Q_c expression is shown correctly. The equilibrium will shift to the left because the volume is increased and thus $Q_c > K_c$.	1

position using Q, because he or she forgot to take the change in the number of moles of CS_2 into account. Overall, eight teachers tried to use a quantitative approach to solving the first problem, but only three of them were successful, indicating that we should provide more opportunities for teachers and students to attempt problems involving constant-pressure systems.

The coding results of the second problem are shown in Table 2. Twenty-two of the 33 teachers predicted no change and 12 of them (Code 2B1) cited LCP as their explanation. Eight teachers (Code 2B2) believed that the addition of argon gas will not disturb the position of equilibrium because there is no reaction between argon and any of the chemicals involved in the forward and reverse reactions. This misconception may be due to the statement of LCP in some textbooks such as the one written by Petrucci et al. *(20)*. Because argon is not a *reacting* species in eq 2, some teachers may have thought that argon never disturbs the position of equilibrium. Another possible reason why so many teachers failed to solve the second problem is that many textbook writers just point out that addition of an inert gas to a chemical system at constant volume will not affect the equilibrium position, but they do not explain in terms of the equilibrium law: see, for example, van Kessel et al. *(28)*. Consequently, the effect of inert gases on chemical equilibrium is rarely discussed in chemistry classrooms. Three teachers (Codes 2C1 and 2C2) predicted a shift in equilibrium to the right based on the “change-then-offset” logic of LCP. One teacher (Code 2A4) appeared to apply the logic of LCP and predicted a left shift of the equilibrium position, ignoring the fact that total gas pressure in the reactor is kept constant.

Only four teachers (Code 2A1) answered the second problem correctly based on the equilibrium law or Q. One possible reason is that in Hong Kong, few textbook writers discuss the effect of inert gases on chemical equilibrium. The Q_c expression for eq 2 is

$$Q_c = \frac{\left(\dfrac{n_{CH_3OH}}{V}\right)}{\left(\dfrac{n_{CO}}{V}\right)\left(\dfrac{n_{H_2}}{V}\right)^2} = \frac{n_{CH_3OH}\, V^2}{n_{CO}\, n_{H_2}^{\;2}} \qquad (5)$$

The volume, V, increases after argon gas is added at constant pressure and temperature. As a result, Q_c is greater than K_c. The position of equilibrium must shift to the left.

The coding results of the third equilibrium problem are summarized in Table 3. A total of 14 teachers (Code 3B1) focused on the increase in total pressure in the system and relied on LCP to make their predictions. Since LCP predicts a left shift in equilibrium forming less NO_2 molecules, these teachers thought that the *concentration* of NO_2 in the mixture must be lower than the original value when the equilibrium is re-established. They did not pay attention to the change in volume. Two teachers (Code 3C1) did take the volume change into account, but they argued that the concentration of NO_2 in the new equilibrium mixture is not certain because both the volume and number of NO_2 molecules decrease. Four teachers (Code 3B2) also considered the decrease in volume and argued that the equilibrium must shift to produce less gaseous molecules. Three teachers (Code 3B3) argued that the concentration of NO_2 must increase initially as the volume is reduced, and they applied LCP mechanically to predict that the equilibrium will shift to the left to relieve this change. They did not recognize that when the volume is reduced, instantaneously both the concentrations of NO_2 and N_2O_4 will increase.

All of the above teachers’ predictions contradict the experimental fact; that is, the concentration of NO_2 in the new

Table 2. Coded Responses to the Second Equilibrium Problem

Code	Teacher Response	Number of Teachers
2A1	The position of equilibrium will shift to the left. The total volume is included in the K_c or Q_c expression to predict the equilibrium shift correctly.	4
2A2	The equilibrium will shift to the left. The concentrations of all gases will decrease due to an increase in volume. But the K_c expression is written incorrectly.	1
2A3	The equilibrium will shift to the left. According to the ideal gas equation, the volume will increase. No further explanation.	1
2A4	The equilibrium will shift to the left. Addition of argon will increase the volume and lower the total gas pressure in the reactor. There are more molecules on the left hand side of the chemical equation. Therefore, the equilibrium will shift to the left to increase the total gas pressure in the reactor.	1
2A5	The equilibrium will shift to the left. Addition of argon will lower the partial pressures of CO, H_2, and CH_3OH. The equilibrium will shift to increase the total pressure of the system.	1
2B1	No equilibrium shift. According to LCP, if an equilibrium system is subjected to a change in reactants or products, it will shift to counteract/oppose/minimize/relieve the change. But argon is not involved in the reaction.	12
2B2	No equilibrium shift, because argon does not react with any of the chemicals in the mixture.	8
2B3	No equilibrium shift because argon gas will not affect the partial pressures or concentrations of chemicals in this system.	1
2B4	No equilibrium shift. But no explanation was given.	1
2C1	The equilibrium will shift to the right. According to LCP, the system should adjust to minimize the increase in the number of gaseous molecules.	1
2C2	The equilibrium will shift to the right to minimize the increase in volume.	2

equilibrium mixture will be higher than its initial concentration prior to the movement of the plunger. Only two teachers (Code 3A1) answered the third problem correctly using the equilibrium law:

$$K_c = \frac{[NO_2]_{eq}^{\,2}}{[N_2O_4]_{eq}}$$

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{n_{NO_2}}{V}\right)^2}{\left(\frac{n_{N_2O_4}}{V}\right)} = \frac{n_{NO_2}^{\;2}}{n_{N_2O_4}\,V} \qquad (6)$$

When the volume, V, is decreased at constant temperature, Q_c is greater than K_c and thus the equilibrium must shift to the left. As a result, the number of N_2O_4 molecules will increase. Because the volume is reduced, the concentration of N_2O_4 in the new equilibrium mixture must increase. To keep K_c constant, the concentration of NO_2 in the new equilibrium mixture must be higher than that in the initial equilibrium mixture. Although four teachers (Code 3A2) also pointed out that the concentration of NO_2 will increase when the new equilibrium is re-established, they predicted that the equilibrium must shift to the right.

Conclusions and Implications

Chemistry educators worldwide have long been asking the question: How do we best help secondary or college students understand the principles of chemical equilibrium? Students are always considered to be the source of problems whenever they have misconceptions about chemical equilibrium after teacher instruction. However, the misconception test administered in this study revealed that most of the 33 teachers failed to solve chemical equilibrium problems owing to their reliance on the "change-then-offset" logic of LCP. There was no discernible pattern as to whether more experienced teachers performed better on the misconception test than less experienced ones. Only three teachers understood that the addition of more CS_2 gas at constant pressure and temperature can shift the equilibrium in eq 1 to the reactant rather than the product side. Only four teachers understood that the addition of argon gas at constant pressure and temperature will decrease the concentration of every gas in eq 2 and change its position of equilibrium. Only two teachers applied the equilibrium law successfully to predict that when the volume of the equilibrium in eq 3 is decreased at constant temperature, the concentration of NO_2 gas will increase in the new equilibrium state. These findings are alarming in view of the supposedly strong knowledge base of chemistry teachers in Hong Kong but consistent with those found in other countries *(18, 25, 27)*. This study has provided solid evidence of the adverse effects of LCP on teacher understanding of chemical equilibrium.

No doubt, the most important implications of the research reported in this article have to do with curriculum content and chemistry teacher education. Secondary students find chemical equilibrium very difficult not only because the concepts of chemical equilibrium are abstract but also because there are problems in the selection of curriculum content. The inclusion of LCP in the school chemistry curriculum does not meet two important criteria for selecting curriculum content: significance and validity *(29, 30)*. Significance refers to the extent to which the selected content is essential to the topic under study and enables students to engage in learning in meaningful ways. Validity

Table 3. Coded Responses to the Third Equilibrium Problem

Code	Teacher Response	Number of Teachers
3A1	The concentrations of NO_2 will increase. The volume is included the K_c or Q_c expression correctly. Because $Q_c > K_c$, the position of equilibrium must shift to the left. Both the concentrations of N_2O_4 and NO_2 will increase when the equilibrium is re-established.	2
3A2	The concentration of NO_2 will increase. More molecules are present on the right hand side of the equation. LCP predicts that the equilibrium must shift to the right to counteract/oppose/minimize/relieve the decrease in volume.	4
3B1	The concentration of NO_2 will decrease. LCP predicts that the equilibrium must shift to the left to counteract/oppose/minimize/relieve the increase in total pressure.	14
3B2	The concentration of NO_2 will decrease. If the volume is decreased, the equilibrium must shift to produce less molecules. The equilibrium position will shift to the left.	4
3B3	The concentration of NO_2 will decrease. Because the volume is reduced, the concentration of NO_2 must increase instantaneously. LCP predicts that the equilibrium must shift to the left to relieve this change.	3
3C1	The concentration of NO_2 is not certain. LCP predicts that the equilibrium must shift to the left to counteract/minimize the increase in total pressure. But both the volume and number of NO_2 molecules decrease.	2
3D1	No comments on the concentration of NO_2. The K_c or Q_c expression is shown correctly. The equilibrium will shift to the left.	2
3D2	No comments on the concentration of NO_2.The equilibrium will shift to the left to compensate for the decrease in volume.	2

is concerned about the accuracy of the content. LCP does not open the door of learning opportunities for students; rather it deters their meaningful learning of chemistry because application of LCP may result in inaccurate predictions.

LCP is largely a content issue rather than a pedagogical issue in chemistry education if we intend to promote real learning of chemical equilibrium in school. For secondary chemistry courses, the most promising change in the content of the chemical equilibrium topic would be to replace LCP by reaction quotient and a simplified version of the van't Hoff equation *(14)*. Unfortunately, the chemistry curricula prepared by examination boards in many countries recommend high school or secondary teachers to teach only LCP. For example, in Australia, the Board of Studies *(31)* has included only LCP in the chemistry syllabus. Therefore, educating chemistry educators worldwide, including teacher educators, textbook writers, and school teachers, on the inadequacy of LCP should be a high priority.

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